Critical Overlap Concentration of Poly(n-butyl methacrylate) in Ionic Liquid and Methylcellulose in Water

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Abstract

In this study, intrinsic viscosity measurements were applied to determine critical overlap concentration c* for two systems with lower critical solution temperature (LCST) phase behavior: poly(n-butymethacrylate) (PnBMA) in ionic liquid bis(trifluoromethylsulfonyl)imide ([BMIm][TFSI]), and methylcellulose in water. The c* of both polymers was found to exhibit strong dependence on molecular weight and temperature.

Introduction

Critical overlap concentration (c*) is one of the most important characteristics for a polymer solution. It is the concentration threshold where neighboring polymer coils in the solution start to be involved in frictional interactions.

Ionic liquids (ILs) are organic compounds that exist in an ionic salt form and stay in the liquid phase over a wide range of temperatures. They are interesting solvents with several appealing properties including high thermo-stability and negligible vapor pressure. In this work 1-butyl-3-methylimidazolium: bis(trifluoromethylsulfonyl)imide ([BMIm][TFSI]) is used as solvent to study poly(n-butyl methacrylate) (PnBMA), as a continuation of the research in lower critical solution temperature (LCST) phase behavior of PnBMA in ionic liquids.

Methylcellulose (MC) is a hydrophobically modified cellulose by partially substituting hydroxyl groups with methoxide groups. It is non-toxic, environmentally friendly and sustainable. Currently, it is a common thickener and emulsifier widely applied in food and cosmetics industry.

Methods

Viscosity of dilute polymer solutions η, increases with polymer concentration:

$$\eta = \eta_s(1 + [\eta]c + k_H[\eta]^2c^2 + \cdots)$$

We measure the solvent viscosity η_s and η of a set of polymer solutions with varying concentrations c. $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient.

A modification of the equation above gives

$$\frac{\eta - \eta_s}{\eta_s \mathrm{c}} = [\eta] + k_H[\eta]^2\mathrm{c} + \cdots$$

known as the Huggins equation, based on which a plot of $\frac{\eta-\eta_s}{\eta_s \mathrm{c}}$ vs. c gives the y-intercept of $[\eta]$.

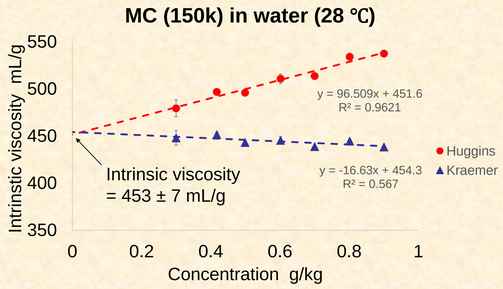
Likewise, Kraemer's equation is used in the same manner:

$$\frac{\ln(\eta/\eta_s)}{c} = [\eta] + k_K[\eta]^2\mathrm{c} + \cdots$$

Finally, we could determine the c* from our measured intrinsic viscosity data by the following relation:

$$c^* = \frac{3 \times 6^{\frac{3}{2}}\Phi}{4\pi N_A[\eta]}$$

where $\Phi = 2.25 \times 10^{23}\ mol^{-1}$



Measurements

Viscosities of [BMIm][TFSI] solutions were found to be approximately 50 to 65 centipoise, for this range, an AR-G2 Rheometer was used.

AR-G2 Rheometer

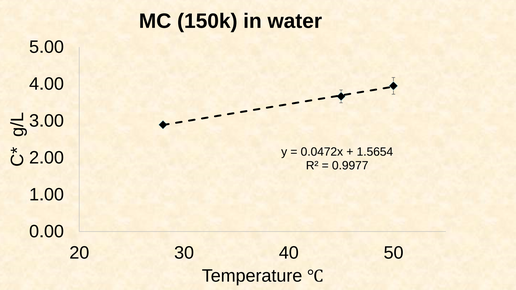
MC water solutions' viscosity ranges from 1.0 to 1.4 centipoise. An appropriate choice of instrument for this viscosity range would be a capillary viscometer immersed in water bath.

Bathed Capillary Viscometer

Result

c* at 23.3 °C of PnBMA in [BMIm][TFSI] was found to be around 3.5 wt% for 47k PnBMA and 5 wt% for 84k PnBMA. However the uncertainties, possibly due to impurities in the samples, were on order of 40%.

The measurements for methylcellulose gave accurate result. A linear correlation of c* with temperature was observed for 150k MC shown as below.



Determination of c* is very "error sensitive", a 1% error in solvent viscosity could propagate to approximately 20% error in the value of c*.

Knowledge of c* as a function of temperature and molecular weight will provide information about the thermodynamics of the polymer solutions, and will inform the experimental design of future investigations of the phase behavior.

Selected References

1. Lott, Joseph R., et al. "Fibrillar Structure in Aqueous Methylcellulose Solutions and Gels." *Macromolecules* (2013).

2. Hoarfrost, Megan L., Yanpu He, and Timothy P. Lodge. "Lower Critical Solution Temperature Phase Behavior of Poly (n-butyl methacrylate) in Ionic Liquid Mixtures." *Macromolecules* 46.23 (2013): 9464-9472.

Acknowledgement

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